

Transport and magnetic anomalies due to A-site ionic-size mismatch in $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$

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Abstract. We present the results of measurements of the electrical resistivity (ρ), magnetoresistance (MR) and dc and ac susceptibility (χ) of polycrystalline samples of the type $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$, synthesized under identical heat-treatment conditions. The substitution of larger Ba ions for Ca results in a *non-monotonic* variation of the Curie temperature (T_C) as the system evolves from a charge-ordered insulating state for $x = 0.0$ to a ferromagnetic metallic state for $x = 0.5$. An intermediate composition, that with $x = 0.1$, interestingly exhibits ferromagnetic, insulating behaviour with thermal hysteresis in the ac χ at around the Curie temperature ($T_C = 120$ K). The $x = 0.2$ and 0.3 compounds exhibit semiconducting-like behaviour as the temperature is lowered below 300 K, with a broad peak in ρ at around 80–100 K; these compositions exhibit a weak increase in ρ as the temperature is lowered below 30 K, indicative of electron localization effects; these compositions also undergo ferromagnetic transitions below about 200 and 235 K respectively, though these are non-hysteretic; most significantly, for these compositions, the MR is large and conveniently measurable over the entire temperature range of measurement below T_C and this experimental finding may be of interest from the applications point of view. We infer that the A-site ionic-size mismatch plays a crucial role in determining these properties.

The observation of large magnetoresistance (MR) in the vicinity of the Curie temperature (T_C) in hole-doped LaMnO_3 systems, both in thin films as well as polycrystals [1, 2], opened up a new direction of research, namely, giant magnetoresistance (see, for instance, references [3, 4]). From the applications point of view, it is desirable [5] to identify systems exhibiting conveniently measurable electrical resistivity (ρ) and a large MR over a wide temperature range. In this sense, the observation of such an effect in polycrystalline thin films as well as in the bulk form (but not in epitaxial thin films and bulk single crystals) of $\text{La}_{2/3}(\text{Ba}, \text{Ca})_{1/3}\text{MnO}_3$ is of considerable interest [5–7]. Apparently, the presence of strains across the grain boundaries is an important deciding factor for such a behaviour [6]. In this respect, we considered it worthwhile to carry out investigations on the series $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$, as there is a large lattice strain induced by the size mismatch between Ca and Ba. Our results reported here establish large magnetoresistances for $x = 0.2$ and 0.3 compositions over a wide temperature range as the temperature is lowered below T_C ; the magnitude of the MR is precisely measurable down to 4.2 K, since these compositions are not insulators at low temperatures in zero field.

There is also another reason for investigating this Ba-substituted series. It is known that the $x = 0.0$ oxide exhibits a charge-ordered (CO) antiferromagnetic (AF) insulating state below 150 K and that the ferromagnetism sets in below 220 K (see the articles cited in reference [8]).

The substitution of a bigger divalent cation, Sr^{2+} , for Ca^{2+} , in the above series, enhances the strength of the double-exchange (DE) interaction; this results in a gradual transformation of the insulating antiferromagnetic CO state into a DE ferromagnetic metal as the Sr concentration is increased, resulting in a monotonic increase of T_C [8]. While the magnetic and transport behaviour sensitively depend on the size of the A-site average ionic radius in general for these perovskites [9], there are few reports emphasizing the role of size mismatch of the ions at the A site on the properties [10, 11]. It is therefore of interest to explore how the properties are modified by a higher degree of lattice strain, which can be induced by substituting Ba for Ca, considering the large variation in the average A-site radius from 1.198 Å to 1.343 Å for $x = 0.0$ and 0.5 respectively (when substituting Ba for Ca).

At this juncture, we would like to remark that there is very little work in the literature on the influence of Ba substitution for Ca in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. In fact, systematic studies on $\text{R}_{1-x}\text{Ba}_x\text{MnO}_3$ (R = rare earth) are also scarce, which prompted Barnabe *et al* [12] to investigate the phase transitions and magnetoresistance in the R = La series, though there are some reports on specific compositions with x close to $x = 0.3$ (references [6, 7, 9, 13–17]). It is also to be noted that the magnetic behaviour of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ is extremely sensitive to the sample preparation conditions and impurities and that the magnetic phase diagram is very complex around $x = 0.5$ (see, for instance, [8, 18–20]). Therefore, it is absolutely essential to keep the starting materials and sample preparation conditions the same for a series of compounds, if one has to compare the properties of several compositions within such a series. We have therefore taken sufficient care in the present investigation in this respect.

Polycrystalline samples of the series, $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5), have been prepared by a standard solid-state reaction route using the required amounts of high-purity (better than 99.9%) La_2O_3 , CaCO_3 , BaCO_3 and Mn_2O_3 with heat treatment similar to that mentioned in reference [19], except that the final sintering was continued for seven days. We had to perform the final sintering for such a long duration, as otherwise the ferromagnetic transitions in these compounds are found to be spread over a wider temperature range. The x-ray diffraction patterns taken with Cu $K\alpha$ radiation are shown in figure 1; the positions of the diffraction lines and the lattice constants derived from these patterns (table 1) clearly highlight systematic lattice expansion with the substitution of Ba for Ca. The data were analysed by the Rietveld method using the program FULLPROF [21]. We find that the samples are single phase for $x < 0.4$, forming in an orthorhombic structure with the space group $Pnma$ (reference [22]). For higher- x compositions there are additional weak lines which appear to arise from an extra phase, identified as BaMnO_3 (also see reference [20]); it appears that, even for $x = 0.5$, we are able to retain orthorhombic structure, in contrast to the cubic structure reported by Barnabe *et al* [12], and this discrepancy is attributed to

Table 1. Lattice parameters, average A-site ionic radius ($\langle r_A \rangle$), tolerance factor (t), variance (σ^2) of the A-site ionic size and Curie temperature (T_C) for the $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$ compounds. The σ^2 -values for the Sr compounds are also given. The errors in the lattice parameters are estimated to be 0.004 Å.

x	a (Å)	b (Å)	c (Å)	$\langle r_A \rangle$	t	$\sigma^2(\text{Ba})$ ($\sigma^2(\text{Sr})$)	T_C (K)
0.0	5.413	7.631	5.424	1.198	0.923	0.0003 (0.0003)	250
0.1	5.437	7.655	5.461	1.227	0.933	0.0069 (0.0014)	120
0.2	5.487	7.713	5.501	1.256	0.944	0.0117 (0.0021)	200
0.3	5.480	7.731	5.509	1.270	0.954	0.0148 (0.0025)	235
0.4	5.499	7.759	5.511	1.285	0.965	0.0163 (0.0025)	300
0.5	5.522	7.793	5.533	1.314	0.976	0.0162 (0.0022)	340

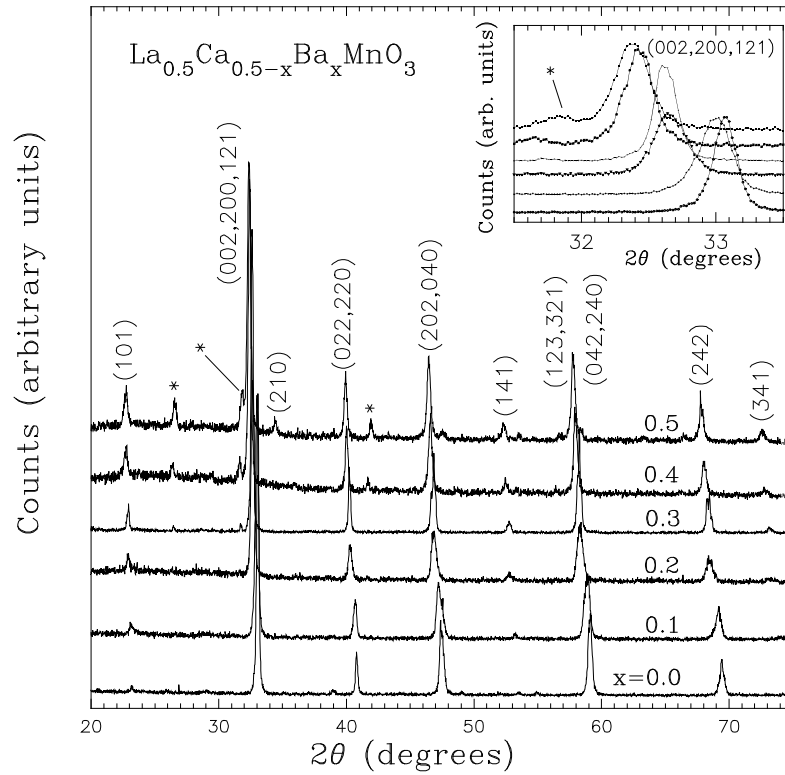


Figure 1. X-ray diffraction patterns at 300 K of some of the compositions of the series $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$. The asterisks for Ba-rich compositions mark the lines arising from an extra phase, presumably due to BaMnO_3 . The patterns around the most intense lines are shown in an expanded form in the inset.

the different sample preparation conditions. In fact, the value of the well-known ‘tolerance factor’ ($t = [r_A + r_O]/\sqrt{2[r_B + r_O]}$, a measure of the deviation of the ABO_3 perovskite structure from cubic structure), listed in table 1 for all compositions, is 0.976, well below unity for this composition. Therefore, it is not unnatural that this composition is non-cubic. The ρ -measurements were done by a four-probe method in the presence and in the absence of a magnetic field (H) employing a conducting silver paint for electrical contacts; the measurements of the magnetoresistance ($\text{MR} = \Delta\rho/\rho = [\rho(H) - \rho(0)]/\rho(0)$) were performed in the longitudinal mode. Direct-current magnetic susceptibility (χ -) measurements ($H = 2000$ Oe and 100 Oe; zero-field cooled (ZFC)) were performed employing a superconducting quantum interference device (SQUID) in the temperature range 4.2–350 K; the data for the field-cooled (FC) state of the specimens were also collected in the presence of $H = 100$ Oe; isothermal magnetization (M -) measurements were performed at 4.2 K up to 55 kOe. Alternating-current χ -measurements (4.2–350 K), with a frequency of 105 Hz and a driving field of 0.8 Oe, were also performed both while cooling and while warming the samples.

The results of the ρ -measurements are shown in figures 2 and 3. As stated in the literature, the $x = 0.0$ compound shows insulating behaviour as a result of which the values of ρ below 50 K are not measurable; however, the application of a field H , of say 30 kOe, results in a significant reduction of low-temperature ρ due to the melting of the CO state (figure 3(a)). The

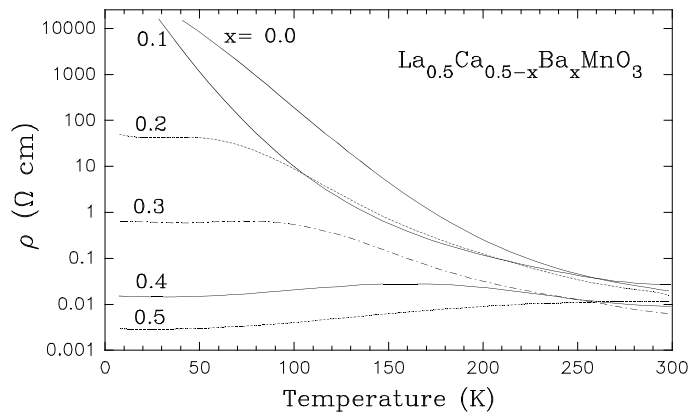


Figure 2. The electrical resistivity (ρ) as a function of temperature for some of the compounds $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$.

same is qualitatively the case for $x = 0.1$ as well (see figure 3(b)). However, no significance should be attached to the tendency of ρ for $x = 0.0$ to level off at low temperatures (below 100 K) in figure 2, as it is rather difficult to measure such large ρ -values reliably by a dc resistivity method. Further substitution of Ba results in gradual reduction of ρ (see figure 2), showing the transformation of the insulating ($x = 0.0$) state to a metallic ($x = 0.5$) phase. The intermediate compositions (with $x = 0.2, 0.3$ and 0.4) each exhibit a negative temperature coefficient of ρ (semiconducting-like) below 300 K followed by a broad hump—at around 50, 100 and 200 K respectively; these humps possibly arise from grain boundary effects [6, 7]. Thus, the resistivity values, though large, are in the convenient range of measurement down to 4.2 K even in zero field, unlike the case for $x = 0.0$ and 0.1 compounds. It is to be noted that, for the $x = 0.2$ and 0.3 compounds, there is a weak increase in ρ at low temperatures ($T < 30$ K; see figure 3(c)). Recently, there have been reports [6, 7] on A-site mismatch-induced electron localization in some of the rare-earth manganites. The relevant parameter which characterizes this disorder is the variance (σ^2) (reference [17]) of the ionic radii at the A site, and this parameter is rather large for doping with $x = 0.2$ and 0.3 Ba as compared to Sr (see table 1). Hence, disorder-induced electron localization effects may be operative in the Ba-substituted compounds. The application of a magnetic field for these intermediate compositions depresses the magnitude of ρ at low temperatures and it must be emphasized that the magnitude of this depression is larger at temperatures far below the respective T_C -values (see below). Clearly, the magnitude of the (negative) MR is large and precisely measurable in the temperature range 4.2–100 K (–70 to –80%; see figure 3(c), inset) for these compositions, unlike the situation for $x = 0.0$ and 0.1 . Following the arguments in references [6] and [7], we attribute the low-temperature enhancement of the MR to size-mismatch effects across the grain boundaries. When measured as a function of H at 4.2 K, ρ undergoes a sharp drop for the initial application of H due to the dominant scattering response across grain boundaries, followed by a slower fall with further increase of H (figure 3(d)). The MR exhibits hysteretic behaviour, apparently due to such grain boundary effects in ferromagnets. For the compositions at the Ba-rich end, which are metallic, there is no noteworthy feature in the MR and hence we do not present these results here.

In order to understand the magnetism of these oxides better, we have performed magnetization studies as well. In the dc χ - T data (figure 4), we find a sharp increase of χ for all of the compositions below a certain temperature, attributable to the onset of ferromagnetic ordering.

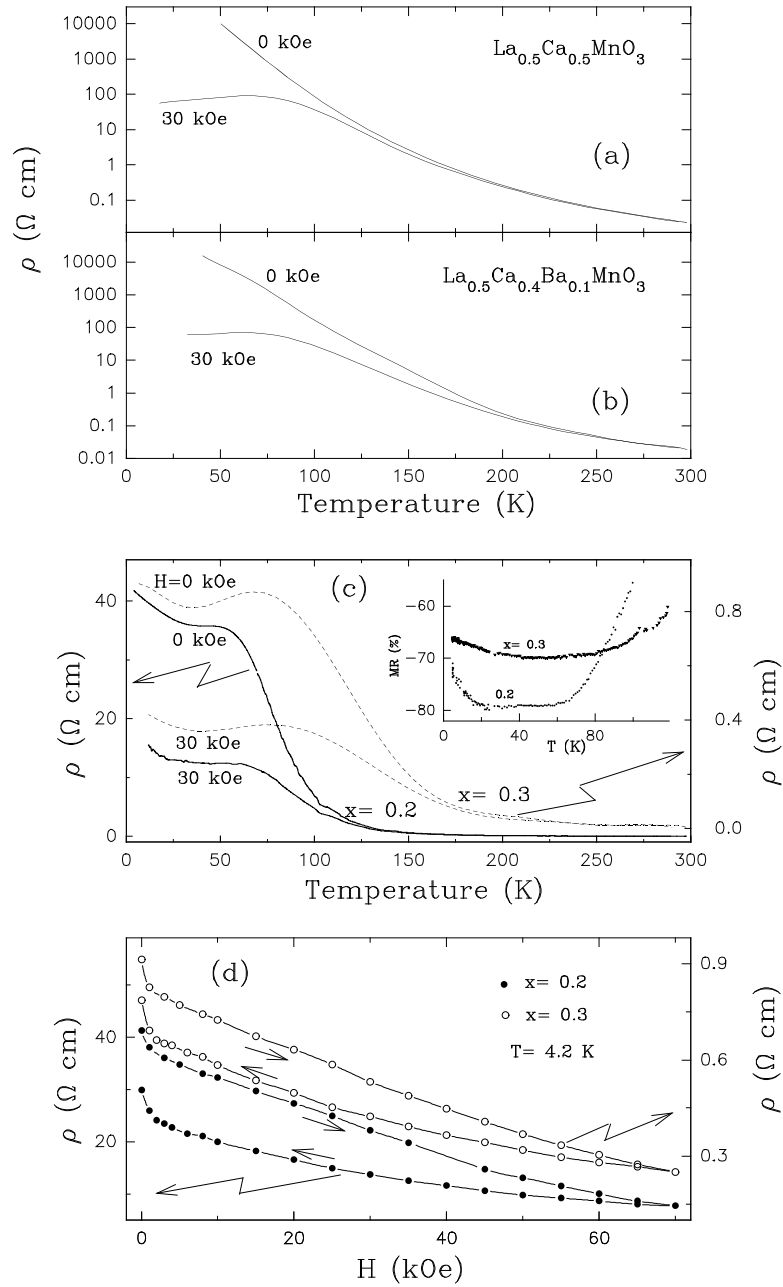


Figure 3. The temperature-dependent electrical resistivity (ρ) behaviour for $x = 0.0, 0.1, 0.2$ and 0.3 samples of the series $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$, in zero magnetic field and in a field of 30 kOe, is shown in (a), (b) and (c). The temperature-dependent magnetoresistance for $x = 0.2$ and 0.3 is shown in the inset of (c). ρ as a function of the magnetic field (H) at 4.2 K for $x = 0.2$ and 0.3 is shown in (d).

The value of T_C inferred from this rise (at around 250, 120, 200, 235, 300 and 340 K for $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5) undergoes non-monotonic variation with Ba substitution.

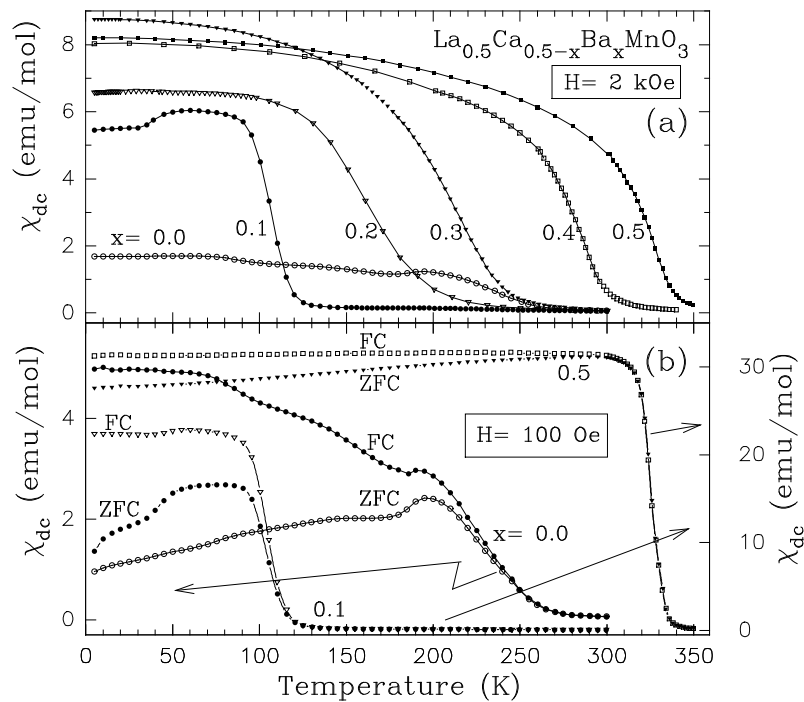


Figure 4. (a) The dc magnetic susceptibility (χ) as a function of temperature measured in a magnetic field of 2 kOe and (b) typical zero-field-cooled and field-cooled χ -behaviour measured in a field of 100 Oe, for some of the compounds $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$.

Even if the heat treatment is the same as that employed in reference [8], we see a similar trend, though these transitions are very broad for such short-time heat treatments. It may be recalled that, for the Sr-substituted samples [8], T_C monotonically increases with x , which is consistent with the well-known direct relationship between A-site ionic size and DE-mediated ferromagnetism. The breakdown of this relationship in the present series should arise from the strains in the lattice induced by initial Ba substitution. We therefore interpret the observed non-monotonic trends in T_C for the Ba-substituted compounds in terms of a competition between the disorder-induced electron localization and an enhancement of the DE-induced ferromagnetism resulting from an increase in the angle subtended by Mn–O–Mn bond and/or a decrease in the O 2p covalent mixing strength with increasing Ba concentration [10]. Similar non-monotonic variation of T_C due to size-mismatch effects has been found, to our knowledge, in only one system, namely, $\text{Pr}_{0.5}(\text{Ba}, \text{Sr})_{0.5}\text{MnO}_3$ (reference [11]) and, in this sense, our finding gains importance.

We note the following minor discrepancies between the observed values of T_C and those reported in the literature for the two end members:

- It is well known [8, 19] that the $x = 0$ compound orders ferromagnetically at 225 K. The slightly higher T_C -value for this composition in the present studies, evident from the rise below 250 K in the dc χ (see figure 4(a)) as well as in the ac χ (appearing in the form of a hump below 250 K in figure 5) must be due to different heat-treatment conditions, as the starting raw materials are the same as those employed in reference [8]. It should be noted that the feature due to the ferromagnetic transition as observed in ac χ studies is

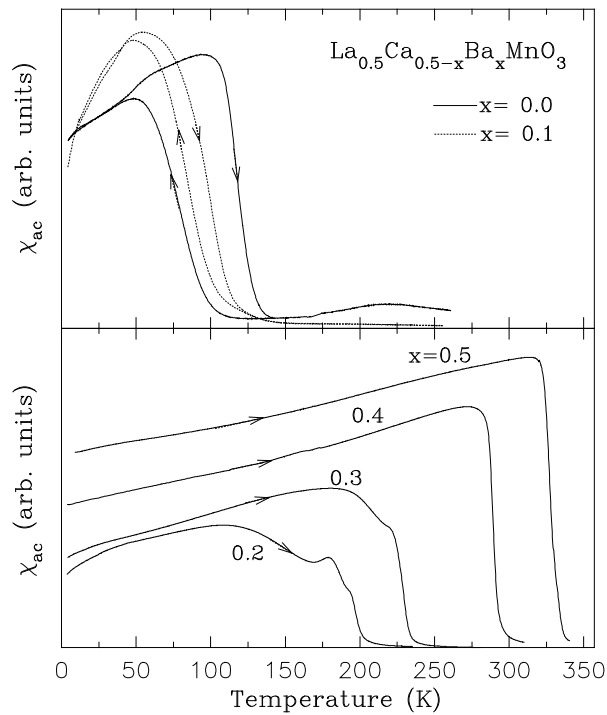


Figure 5. Temperature-dependent ac susceptibility behaviour, for some of the compounds $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$. For two compositions, those with $x = 0.0$ and 0.1 , we observe hysteresis behaviour while cooling and warming (shown separately in the upper part of the figure).

less prominent as compared to that observed in dc χ studies; presumably the application of H amplifies the feature in the latter case.

- (b) Our T_C -value for $x = 0.5$ is larger than that reported (about 290 K) by Barnabe *et al* [12], which could be attributed to our sample having cubic structure as mentioned earlier. It may be added that, on the basis of investigations on $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_3$, Ju and Sohn [6] conclude that oxygen deficiency lowers the value of T_C and hence we believe that the oxygen non-stoichiometry (deviation from 3) is less for our samples.
- (c) For $x = 0.0$, we note that the drop in χ due to the onset of antiferromagnetism below 150 K (references [8] and [19]) is virtually absent, though the reduced magnitude of the high-field magnetization (see below) is indicative of the existence of an antiferromagnetic component; presumably, the present sample preparation conditions induce canting in the spin structure inducing a ferromagnetic component for this composition even below about 150 K; this low-temperature ferromagnetic component cannot be of DE-mediated type, unlike the one setting in at around 250 K, as otherwise one should have observed metallicity at low temperatures.

There are also other interesting features in the dc and ac magnetization data:

- As is well known, the ac χ shows (figure 5) hysteretic behaviour while cooling and warming in the temperature range 75–140 K for $x = 0.0$ due to first-order nature of the charge-ordered antiferromagnetic transition [8]. Interestingly, the same hysteretic behaviour is seen for $x = 0.1$ as well at around the temperature at which there is an onset

of *ferromagnetic* ordering. It is not clear whether this signals the persistence of CO at around 100 K for this composition as well (this temperature is nearly the same as T_C !) In any case, our data seem to provide evidence for the first-order nature of the ferromagnetic transition—similar to the observation for $\text{La}_{0.52}\text{Gd}_{0.15}\text{Ca}_{0.33}\text{MnO}_3$ (reference [23]); this behaviour is not so common among the family of Mn-based perovskites.

- It is interesting to note that the composition with $x = 0.1$ is insulating and hence this sample is not a DE-mediated ferromagnet. Thus this series provides an opportunity to traverse from a spin-canted, charge-ordered, insulating state to a metallic, DE ferromagnet via a (charge-ordered?) insulating ferromagnet by varying the Ca/Ba ratio.
- The isothermal magnetization (M) (figure 6) rises sharply for initial applications of H (below 10 kOe) for all compositions. M saturates to a value close to $3.1 \mu_B$ for all compositions, except for $x = 0.0$, typical of that known for the ferromagnets of this class of Mn perovskites; the values are however low (close to $1 \mu_B$) at high fields for $x = 0.0$, without saturation even at high fields; this observation supports our earlier remark that this alloy is essentially a canted antiferromagnet for the present sample preparation conditions. It is interesting to note that in the Sr-doped compounds [8], the low-temperature antiferromagnetic state is enhanced for initial Sr substitution (up to $x = 0.2$), whereas for Ba doping, $x = 0.1$ is sufficient to depress the antiferromagnetism.

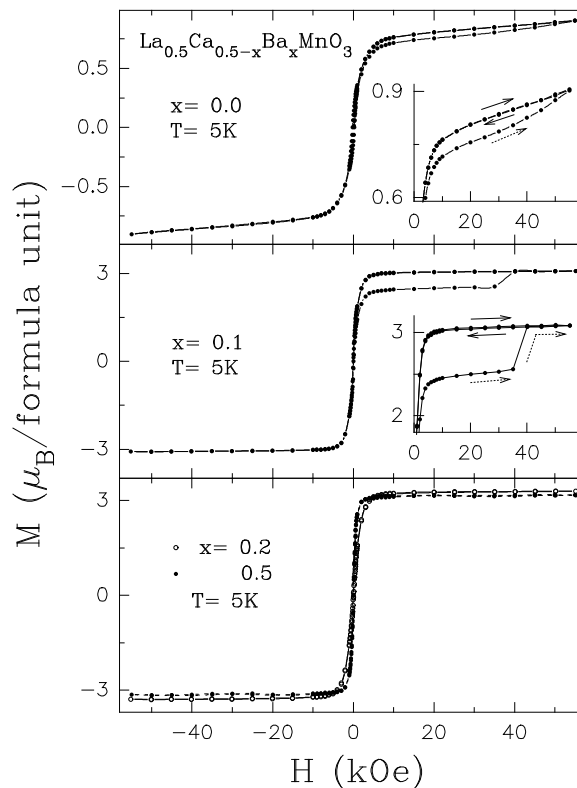


Figure 6. Isothermal magnetization behaviour at 4.2 K for the series $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$. The data for $x = 0.4$ are practically the same as those for $x = 0.5$. For $x = 0.0$ and 0.1 , the deviation of the field-cycled magnetization from the initial magnetization (that is, for increasing magnetic field) is shown in the insets.

If an antiferromagnetic interaction coexists with ferromagnetism for $x(\text{Ba}) = 0.1$, it may occur below 50 K as is evident from the shoulder in the ZFC dc and ac magnetization (see figures 4 and 5). However, this component is suppressed/modified by the presence of H or field cycling. Further observations made below lend additional support to this view and the canted nature of the low-temperature magnetic structure.

- In the $M-H$ plots (figure 6), for $x = 0.0$ and 0.1 , as the field is increased, there is a strong irreversibility between the initial magnetization while increasing the field in the first cycle and the one while decreasing the field as well as increasing the field in the second cycle, as shown in figure 6. These features are similar to those reported for $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ (reference [24]). For $x = 0.1$, we observe a more spectacular feature in the sense that, in the initial curve, there is a sudden increase in M at about 35 kOe. We attribute these features to a possible small canting of the magnetic structures, which is presumably altered by the application of H .
- The coercive-field values are found to be typically 100 Oe for $x < 0.3$, beyond which the value is still closer to zero; these values suggest that the samples are soft ferromagnets.
- The ZFC and FC ($H = 100$ Oe) dc χ -curves tend to deviate from each other from a lower temperature compared to the respective T_C -values, presumably due to the anisotropy of the materials (plots are shown for only three compositions in figure 4(b) for the sake of the clarity of the figure). Similar divergencies have been found even for other magnetic materials exhibiting long-range magnetic ordering and hence need not be associated with spin-glass ordering [25]. The percentage of the ultimate divergence at low temperatures, however, decreases with the increase of the Ba concentration, which we attribute to a corresponding decrease of the metastability.

Thus, we have traced the transformation of the CO insulating state ($x = 0$) into a ferromagnetic-like metal ($x = 0.5$) with increasing Ba concentration in $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$, interestingly traversing through an insulating ferromagnetic compound with a non-monotonic variation of T_C with x . We made several interesting observations on the magnetic and transport behaviour of these oxides. For $x = 0.2$ and 0.3 , the magnetoresistance is quite large and precisely measurable over a wide temperature range well below T_C , an observation which may be of importance for applications. We would like to add that, at the time of writing this article, we came across a publication by Zhong *et al* [26] reporting the observation of a large MR over a wide temperature range for another manganite, $\text{La}_{0.55}\text{Dy}_{0.12}\text{Ca}_{0.33}\text{MnO}_3$, and thus there is considerable interest in identifying systems with such properties. The results establish that the A-site ionic-size mismatches play a decisive role as regards the transport and magnetic behaviour of these manganites.

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